



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷: C09K 11/00	A2	(11) International Publication Number: WO 00/44851 (43) International Publication Date: 3 August 2000 (03.08.00)
(21) International Application Number: PCT/GB00/00268 (22) International Filing Date: 31 January 2000 (31.01.00) (30) Priority Data: 9901971.3 1 February 1999 (01.02.99) GB (71) Applicant (for all designated States except US): SOUTH BANK UNIVERSITY ENTERPRISES LTD [GB/GB]; 103 Borough Road, London SE1 0AA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): KATHIRGAMANATHAN, Poopathy [GB/GB]; 14 Sandhurst Avenue, North Harrow, Middlesex HA2 7AP (GB). (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: ELECTROLUMINESCENT MATERIALS (57) Abstract <p>An electroluminescent material which can form electroluminescent devices which emit light in the ultra-violet region of the spectrum which comprises an organic metallic complex of a transition metal, lanthanide or actinide and a polyamine ligand particularly gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd(EDTA)] and gadolinium europium ethylenediaminetetraacetate salts, Gd[Eu(EDTA)]₃.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Electroluminescent Materials

The present invention relates to electroluminescent materials which can emit light in the ultra-violet region of the spectrum and devices made using such materials.

5 Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications and organic polymers have been proposed as useful in electroluminescent devices, but using these polymers it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

10

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

15 In an article in Chemistry letters pp 657-660, 1990 Kido et al disclosed that a terbium (III) acetyl acetonate complex was green electroluminescent and in an article in Applied Physics letters 65 (17) 24 October 1994 Kido et al disclosed that a europium (III) triphenylene diamine complexes was red electroluminescent but these were unstable in atmospheric conditions and difficult to produce as films.

20

The complexes disclosed in these articles had a relatively low photoluminescent efficiency and were only able to produce green or red light and other colours could not be produced.

25 Patent Applications WO 98/58037 and WO 98/55561 disclose electroluminescent materials which emit light in the visible spectrum and disclose electroluminescent devices incorporating these materials.

The wavelength of the emitted light from an organo metallic complex which is an
30 electroluminescent material depends on the metal or metals and the ligands.

In general the shorter the wavelength of the emitted light the harder it is to obtain effective electroluminescent materials and in particular electroluminescent materials which emit light in the ultra-violet region of the spectrum have hitherto not been possible to produce.

5

An electroluminescent material which can emit ultra-violet light would have a range of applications and would enable there to be a source of ultra-violet light without the need for high temperature or complex high energy or vacuum equipment and so could replace such sources of ultra-violet light.

10

For example, there are devices and displays etc. where ultra-violet light is used to excite other materials to cause these other materials to fluoresce in the visible spectrum.

15 We have now devised organo-metallic complexes which can emit ultra-violet light.

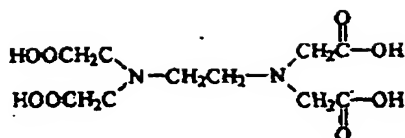
According to the invention there is provided an electroluminescent material which emits light in the ultra-violet region of the spectrum which comprises an organic metallic complex of a transition metal, lanthanide or actinide and a polyamine ligand.

20

The preferred metal is gadolinium in the III state.

Preferred ligands are ethylene diamine tetramine EDTA, DCTA, DTPA and TTHA.

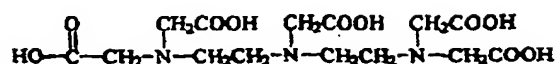
25 The structural formulae of these compounds in the acetic acid form are shown below.



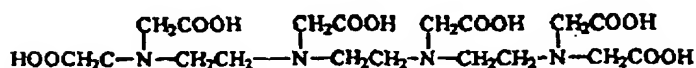
EDTA



DCTA

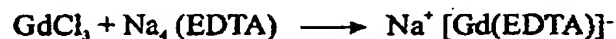


DTPA



TTHA

- 5 The organo metallic complexes can be made by the reaction of gadolinium chloride with an alkali metal salt of the amine e.g. the sodium salt, for EDTA the reaction is



For the other polyamine the corresponding alkali metal salt is used.

- 10 With polyamines which are more than tri-functional e.g. EDTA, DCTA, DTPA, TTHA the complexes can be in the form of a salt e.g. an alkali metal salt and can be used in this form. Alternatively a transition metal, lanthanide or actinide salt e.g. $\text{Ln}^*[\text{Ln}(\text{EDTA})]_3$ where Ln and Ln^* is a transition metal, lanthanide or actinide and preferably a lanthanide e.g. Gd, Sm, Eu, Tb, Dy, etc.

15

Particularly preferred mixed complexes are the gadolinium complexes e.g. $\text{Gd}[\text{Eu}(\text{EDTA})]_3$.

It has surprisingly been found that the lanthanide salts of the organo-metallic complexes exhibit a different electroluminescent spectrum than mixed organo-metallic complexes.

- 5 The mixed lanthanide salts can be made by reacting a lanthanide chloride with a lanthanide polyamine complex.

10 The materials of the present invention can be incorporated into electroluminescent devices which emit ultra-violet light and the invention include such electroluminescent devices.

15 The ultra-violet light emitting devices of the invention comprise a transparent substrate which is a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate. The electroluminescent material can be deposited on the substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend the material for example alcohols such as ethanol, ketones such as acetone and methyl acetylacetonate and chlorinated hydrocarbons such as dichloromethane are suitable in many cases.

20

Alternatively the material can be deposited by spin coating or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

25

In one embodiment there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer. The hole transporting layer serves to transport; holes and to block the electrons, thus preventing electrons from moving into the electrode without

recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

5 Hole transporting layers are used in polymer electroluminescent devices and any of the known hole transporting materials in film form can be used.

10 The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl)-L,L'-biphenyl -4,4'-diamine (TPD), polyaniline etc.

Optionally dyes such as fluorescent laser dyes, luminescent laser dyes can be included so that these dyes fluoresce in the ultra-violet light to give emitted light of a particular colour spectrum.

15 Preferably the electroluminescent material is mixed with a polymeric material such as a polyolefin e.g. polyethylene, polypropylene etc. and preferably polystyrene. Preferred amounts of active material in the mixture is from 95% to 5% by weight of active material and more preferably 25 to 20% by weight.

20 The hole transporting material can optionally be mixed with the electroluminescent material in a ratio of 5-95% of the electroluminescent material to 95 to 5% of the hole transporting compound. In another embodiment of the invention there is a layer of an electron injecting material between the cathode and the electroluminescent material layer, this electron injecting material is preferably a metal complex such as a metal
25 quinolate e.g. an aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron injecting material can be mixed with the electroluminescent material and co-deposited with it.

30 In a preferred structure there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation

layer, the electroluminescent material layer and an electron injection layer which is connected to the anode. The anode can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc.,

- 5 There can be a layer or layers containing a fluorescent material in the device so that the ultra-violet light emitted will cause the material to fluoresce and emit light of a particular colour spectrum.

The invention is described in the following examples.

10

Example 1

Gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd(EDTA)]

Gadolinium chloride (10 mmol) was dissolved in water (5 ml). Ethylenediaminetetraacetic acid, tetrasodium salt hydrate (10 mmol) was dissolved
15 in water (10 ml) and added portionwise to the gadolinium chloride solution. The solution became warm, and after ca. 15 minutes, a white precipitate was formed. The mixture was left for a further 2 hours. The precipitate was filtered off to give a white solid which was washed with water (2 x 5 ml) and dried in air to yield Gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd(EDTA)]

20

Example 2

Gadolinium europium ethylenediaminetetraacetate salts, Gd[Eu(EDTA)]₃

Europium ethylenediaminetetraacetate sodium salt Na[Eu(EDTA)] (4.5 mmol) was dissolved in methanol (30 ml). Gadolinium chloride (1.5 mmol) was dissolved in
25 water (5 ml) and added portionwise to the europium ethylenediaminetetraacetate sodium salt solution. A white precipitate was immediately formed. The mixture was left for a further 1 hour. The precipitate was filtered off to give a white solid which was washed with methanol (2 x 10 ml) and dried in air to yield the product Gadolinium europium ethylenediaminetetraacetate salts, Gd[Eu(EDTA)]₃.

30

Photoluminescence was excited using 325nm line of Liconix 4207 NB, He/Cd laser. The laser power incident at the sample (0.3mWcm^{-2}) was measured by a Liconix 55PM laser power meter. The radiance calibration was carried out using Bentham radiance standard (Bentham SRS8, Lamp current 4,000A, calibrated by National Physical laboratories, England. The PL studies were carried out on samples or films. The Complexes of the examples were tested and the results shown in the Spectra attached as Figs. 1 and 2.

An electroluminescent device constructed with a film of the compounds of examples 1 and 2 with an indium coated glass as anode and an aluminium cathode emitted light in the ultra-violet spectrum when a low voltage was applied across the film. The light was emitted in the same spectrum ranges as in figs. 1 and 2

Claims

1. An electroluminescent material which emits light in the ultra-violet region of the spectrum which comprises an organic metallic complex of a transition metal,
5 lanthanide or actinide and a polyamine ligand.
2. An electroluminescent material as claimed in claim 1 in which the metal is gadolinium in the III state.
- 10 3. An electroluminescent material as claimed in claim 1 or 2 in which the ligand is ethylene diamine tetramine, DCTA, DTPA or TTHA.
4. An electroluminescent material as claimed in claim 3 in which the complex is in the form of a salt .
- 15 5. An electroluminescent material as claimed in claim 4 in which the complex is in the form of an alkali metal salt
6. An electroluminescent material as claimed in claim 4 in which the salt is a
20 transition metal, lanthanide or actinide salt
7. An electroluminescent material as claimed in claim 4 in which the salt is $\text{Ln}^*[\text{Ln}(\text{EDTA})]_3$ where Ln and Ln^* is selected from transition metals, lanthanides and actinides.
- 25 8. An electroluminescent material as claimed in claim 7 in which Ln and Ln^* is selected from Gd, Sm, Eu, Tb, Dy.
9. An electroluminescent material as claimed in any one of claims 1, 4 or 5 in which
30 the metal complex is $\text{Gd}[\text{Eu}(\text{EDTA})]_3$.

10. An electroluminescent device which comprises a transparent substrate on which is deposited an electroluminescent material as claimed in any one of the preceding claims.
- 5 11. An electroluminescent device as claimed in claims 1 to 10 in which the transparent substrate is a conductive glass or plastic material which acts as the anode.
12. An electroluminescent device as claimed in any one of claims 10 to 11 in which there is a hole transporting layer deposited on the transparent substrate and the
10 electroluminescent material is deposited on the hole transporting layer.
13. An electroluminescent device as claimed in any one of claims 10 to 12 in which there is a hole transporting material mixed with the electroluminescent material in a ratio of 5 to 95% of the electroluminescent material to 95 to 5% of the hole
15 transporting compound.
14. An electroluminescent device as claimed in claim 12 or 13 in which the hole transporting layer is an aromatic amine complex.
- 20 15. An electroluminescent device as claimed in claim 14 in which the hole transporting layer is poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD) or polyaniline.
16. An electroluminescent device as claimed in any one of claims 11 to 15 in which
25 there is a metal anode in contact with the electroluminescent material.
17. An electroluminescent device as claimed in any one of claims 10 to 16 in which there is a layer of an electron injecting material between the cathode and the electroluminescent material layer

18. An electroluminescent device as claimed in any one of claims 10 to 17 in which an electron injecting material is mixed with the electroluminescent material and co-deposited with it.

5 19. An electroluminescent device as claimed in claim 17 or 18 in which the electron injecting material is a metal complex or oxadiazole or an oxadiazole derivative.

20. An electroluminescent device as claimed in claim 19 in which the electron injecting material is an aluminium quinolate or 2-(4-biphenyl)-5-(4-tert-butylphenyl)-
10 1,3,4 oxadiazole.

21. An electroluminescent device as claimed in any one of the preceding claims 10 to 20 in which the anode is a metal.

15 22. An electroluminescent device as claimed in claim 21 in which the anode is a aluminium, magnesium, lithium, calcium or a magnesium silver alloy.

23. An electroluminescent device as claimed in any one of the preceding claims 10 to 22 in which there are a plurality of layers of electroluminescent material.

20

24. An electroluminescent device as claimed in any one of the preceding claims 10 to 23 in which there is a layer or layers which incorporates a dye which fluoresces in ultra-violet light to give emitted light in the colour spectrum.

25

1/2

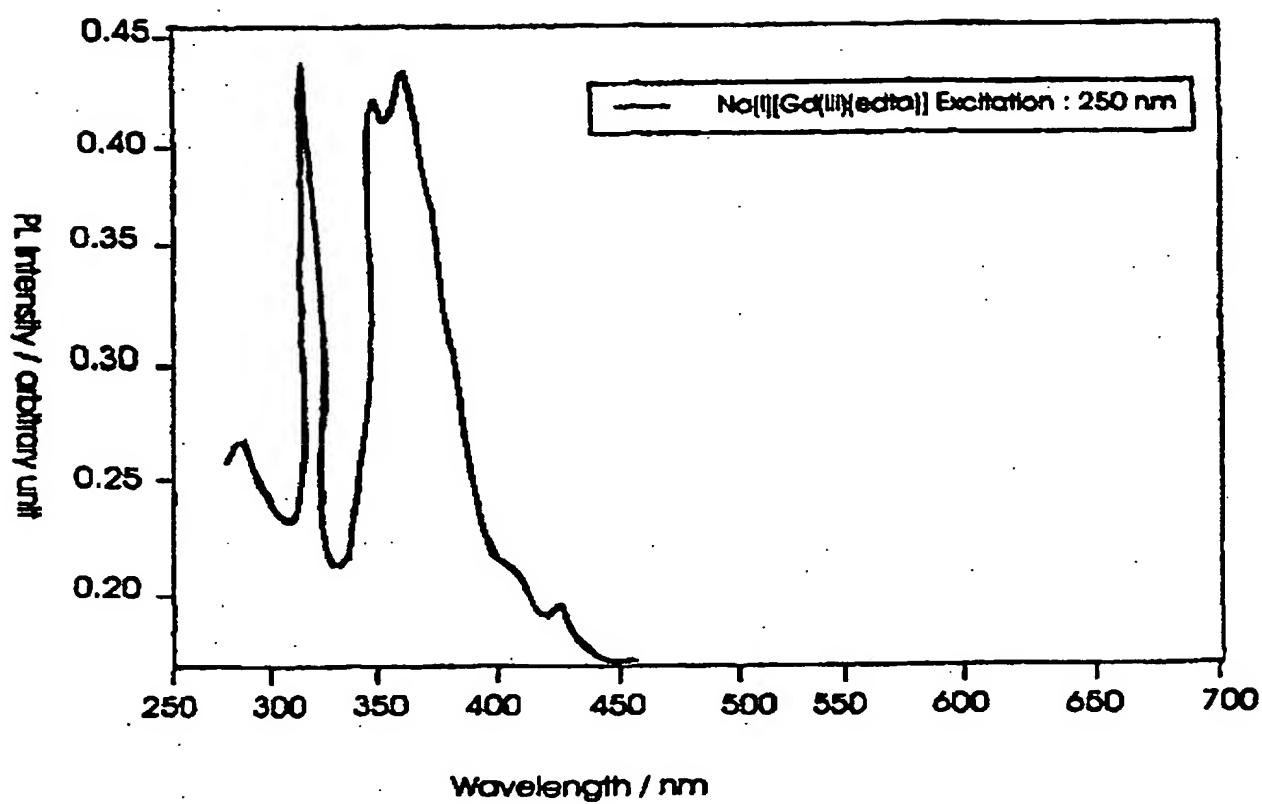


Fig. 1

2/2

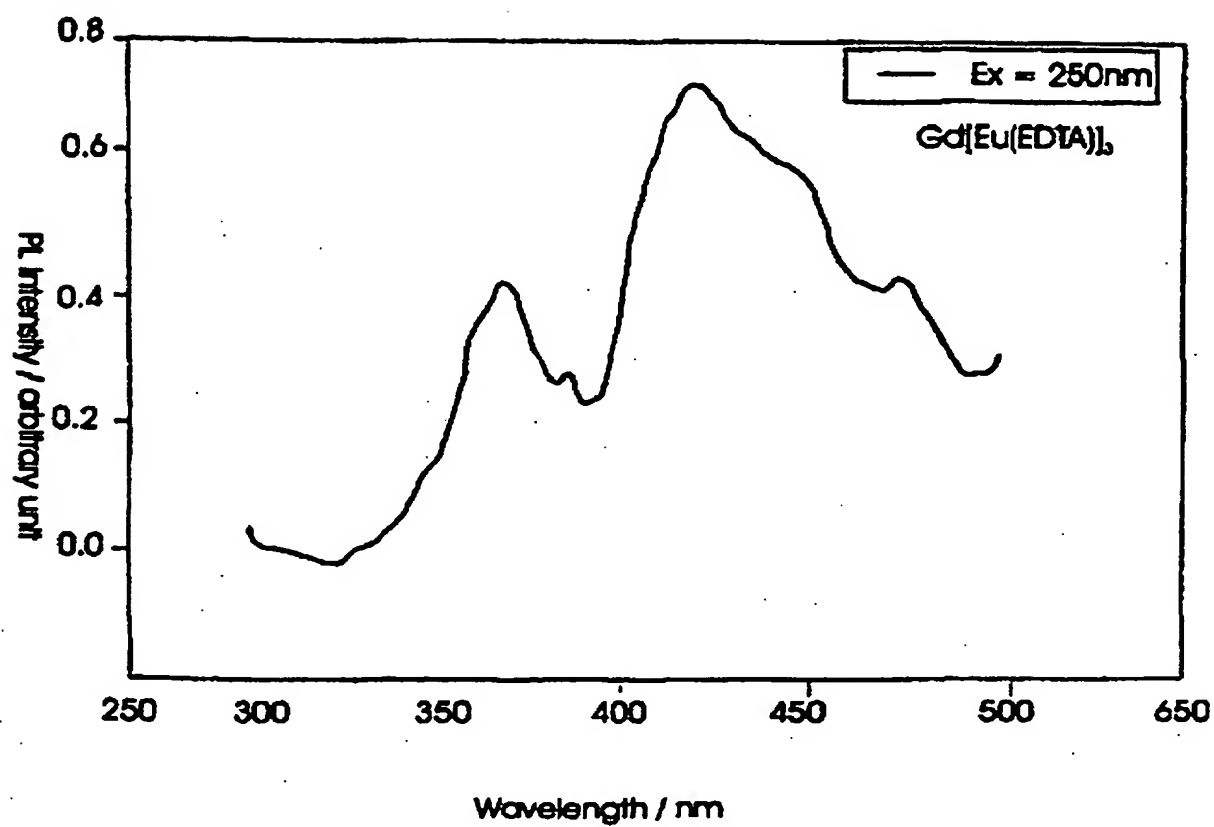


Fig. 2

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 August 2000 (03.08.2000)

PCT

(10) International Publication Number
WO 00/44851 A3

- (51) International Patent Classification⁷: C09K 11/06, H05B 33/14, C07C 229/16
- (21) International Application Number: PCT/GB00/00268
- (22) International Filing Date: 31 January 2000 (31.01.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
9901971.3 1 February 1999 (01.02.1999) GB
- (71) Applicant (for all designated States except US): SOUTH BANK UNIVERSITY ENTERPRISES LTD [GB/GB]; 103 Borough Road, London SE1 0AA (GB).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): KATHIRGA-MANATHAN, Poopathy [GB/GB]; 14 Sandhurst Avenue, North Harrow, Middlesex HA2 7AP (GB).
- (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
- (88) Date of publication of the international search report:
7 December 2000
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROLUMINESCENT MATERIALS

(57) Abstract: An electroluminescent material which can form electroluminescent devices which emit light in the ultra-violet region of the spectrum which comprises an organic metallic complex of a transition metal, lanthanide or actinide and a polyamine ligand particularly gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd(EDTA)] and gadolinium europium ethylenediaminetetraacetate salts, Gd[Eu(EDTA)]₃.

WO 00/44851 A3

INTERNATIONAL SEARCH REPORT

National Application No

PCT/GB 00/00268

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09K11/06 H05B33/14 C07C229/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H05B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TEMPLETON, LIESELOTTE K. ET AL: "Anomalous scattering by praseodymium, samarium and gadolinium and structures of their ethylenediaminetetraacetate (edta) salts" ACTA CRYSTALLOGR., SECT. B (1982), B38(8), 2155-9, XP002139485 table 1	1-5
X	WO 98 55561 A (CHRISTOU VICTOR ; ISIS INNOVATION (GB)) 10 December 1998 (1998-12-10) cited in the application page 7, paragraph 5; claims 1,3,4; examples 9,16 --- -/--	1,2, 10-24

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

13 July 2000

Date of mailing of the international search report

25/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo ru,
 Fax: (+31-70) 340-3016

Authorized officer

Shade, M

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/00268

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARMAROLI N ET AL.; "Luminescence properties of Eu, Tb, and Gd complexes of the hexadentate N-donor podand tris-3-(2-pyridyl)pyrazol-1ylhydroborate" CHEMICAL PHYSICS LETTERS, NL, AMSTERDAM, vol. 5-6, no. 276, 29 September 1997 (1997-09-29), pages 435-440, XP002074915 figures 1,3	1,2
A	WO 98 58037 A (KATHIRGAMANATHAN POOPATHY ; SOUTH BANK UNIV ENTPR LTD (GB)) 23 December 1998 (1998-12-23) cited in the application claims 1-29	10-24
A	"ULTRAVIOLET ELECTROLUMINESCENCE FROM AN ORGANIC LIGHT EMITTING DIODE" ADVANCED MATERIALS, DE, VCH VERLAGSGESELLSCHAFT, WEINHEIM, vol. 7, no. 11, 1 November 1995 (1995-11-01), pages 900-903, XP000537408 ISSN: 0935-9648 the whole document	10-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9855561 A	10-12-1998	AU 7668198 A EP 0988353 A	21-12-1998 29-03-2000
WO 9858037 A	23-12-1998	AU 8116598 A EP 0990016 A	04-01-1999 05-04-2000